**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**
REGION 5
AIR AND RADIATION DIVISION
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

DATE: **MAY 0 4 1994**

SUBJECT: Granville Solvents Inc., Granville, ~~Indiana~~ *Ohio*

TO: Kathleen Warren, Remedial Project Manager
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Office of Superfund (HSRM-6J)

FROM: Daniel L. Meyer, Environmental Engineer
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This memorandum responds to your request for estimated emission rates
at the Granville Solvents source reduction system as a result of both
air sparging and vapor extraction. The air sparging process injects
air into an aquifer. As the air bubbles rise, volatile organic
compounds (VOC) are volatilized from the liquid phase into the gas
phase. Thus, VOCs are stripped from the water. The VOCs
subsequently rise to the surface of the groundwater table along with
the air bubbles. There, the VOCs become trapped between the aquifer
and the vadose zone. There, VOCs will be collected and removed by
vapor extraction wells.

Stripping losses during bubble aeration have been modeled by
Mihelcic, Baillod, Crittenden, and Rogers, "Estimation of VOC
Emissions from Wastewater Facilities by Volatilization and
Stripping," Journal of the Air and Waste Management Association,
Volume 43, January 1993, pages 97-105. Applying the concepts of this
model to available data at the Granville Solvents Inc. Site, I
estimate VOC emissions due to air sparging to be 11 pounds per day.
In modeling VOC emissions, a number a assumptions were made. See
attachment 1 for details.

Still more VOCs have been detected in soil above the groundwater
table. These VOCs naturally migrate up through the soil in the
absence of remedial action. This condition is better understood by
applying emission models. I have applied the methodology found in
the Air/Superfund guidance document entitled, Guideline for

<u>Predictive Baseline Emissions Estimation Procedures for Superfund Sites</u>, January 1992.  Applying this model to the site and given the limited data, I have estimated VOC emissions due to VOC gas migration in the soil to be less than 1 pound per day.  Again, a number of assumptions were made.  See attachment II for details.

If you have any questions regarding these comments, please call at 6-9401.

Attachment(s)

Compounds with relatively low values of H will attain equilibrium with the surrounding liquid relatively quickly after rising only a few meters due to aeration.[1] Accordingly,

$$y_E = HC_E,$$

where $y_E$ = exit gas concentration, H = Henry's law constant (dimensionless), and $C_E$ = effluent concentration. Values for H were obtained from USEPA's Water 7 database. For this air sparging application, assume: 1) Equilibrium is attained relatively quickly for each compound in Table 1, 2) The effluent concentration is equal to the existing groundwater contaminant concentration, 3) The unit operates continuously 24 hours a day, and 4) The air flow rate through entire aquifer is 25 cubic feet per minute. The target compounds along with monitored concentrations, Henry's constant, and exit gas concentrations are tabled below.

## TABLE 1

| Compounds | $C_E$, ($\mu$g/l) | H, ( ) | $y_E$, ($\mu$g/l) |
|-----------|-----------|--------|-----------|
| Benzene | 1 | 0.23 | 0.23 |
| 1,1-Dichloroethane | 200 | 0.63 | 126 |
| cis-1,2-Dichloroethene | 1070 | 0.19 | 203 |
| 1,1,1-Trichloroethane | 2600 | 0.71 | 1846 |
| Tetrachloroethylene | 1300 | 1.19 | 1547 |
| Trichloroethylene | 3300 | 0.37 | 1221 |
| Vinyl Chloride | 20 | 3.53 | 71 |
| trans-1,2-Dichloroethene | 23 | 0.39 | 9.0 |
| 1,2-Dichloroethane | 109 | 0.05 | 5.5 |
| **TOTAL** | | | **5029** |

The estimated total emission rate, E, is equal to:

(Exit gas concentration) x (Air flow rate) x (Efficiency)

$E$ = (5029 $\mu$g/l)(25 ft$^3$/min)(28.3 l/ft$^3$)(1440 min/day)(1 lb/4.54x10$^8$ $\mu$g)
= 11 lb VOC / day.

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[1] Mihelcic, Baillod, Crittenden, and Rogers, "Estimation of VOC Emissions from Wastewater Facilities by Volatilization and Stripping," <u>Journal of the Air and Waste Management Association</u>, Volume 43, January 1993, pages 97-105.

Attachment II
VOC Soil Migration

The amount of soil data has been limited. Due to this lack of information, an important assumption has been made to facilitate the modeling; the VOC concentration in the soil is less than its saturation concentration. Under this scenario, aqueous phase contaminants exist in the vadose zone. Concentrations less than saturation concentration ($C_{sat}$) indicate aqueous phase contaminants within the soil matrix. The term, $C_{sat}$, can be estimated utilizing the following equation based upon A/SF guidance[2]:

$$C_{sat} = \frac{[(k_d)(f_{oc})(\beta)] + [(s)(p_w)] + [(s)(H)(p_a)]}{\beta}$$

where $k_d$ = soil/water partition coefficient, $f_{oc}$ = fraction of organic carbon in soil (dimensionless), $\beta$ = soil bulk density, s = solubility of contaminant in water, $p_w$ = water-filled soil porosity, H = Henry's law constant, and $p_a$ = air-filled soil porosity. The term $f_{oc}$ is typically 0.02. Because a number of the variables determining $C_{sat}$ are unknown, we underestimate $C_{sat}$ to be the product of $k_d$ and $f_{oc}$.

$$C_{sat} = (k_d)(f_{oc})$$

For tetrachloroethylene,

$$C_{sat} = (7.28 \text{ ml/g})(1.624 \text{ g/cm}^3)(100 \text{ cm/m})^3(\text{m}^3/1000\text{l})(1/1000\text{ml})(0.02)$$
$$= 0.24$$

Here, as is also the case with other contaminants in the vadose zone, $C \ll C_{sat}$. See Table 2 for results. Therefore, the assumption of aqueous phase contamination in the vadose zone holds, and an emission rate for VOC migration can be estimated by utilizing the following equation[2]:

$$E = (C)(H)/(k_d),$$

where E = VOC emission rate, C = concentration of VOC in the soil, H = Henry's constant (dimensionless), and $k_d$ = soil/water partition coefficient. In turn,

$$K_d = K_{oc} \times f_{oc},$$

where $K_{oc}$ = organic carbon partition coefficient, and $f_{oc}$ = fraction of organic carbon in soil. A typical value for $f_{oc}$ is 0.02. Values for $K_{oc}$ were obtained from the Superfund Public Health Evaluation Manual, October 1986.

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[2] Guideline for Predictive Baseline Emissions Estimation Procedures for Superfund Sites, January 1992.

Four VOCs have been identified in the soil: tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene, and xylene. These compounds and their respective properties have been tabled below.

## TABLE 2

| Compound | C, (g/g) | $C_{sat}$, (g/g) | H, ( ) | $K_{oc}$, (ml/g) |
|---|---|---|---|---|
| Tetrachloroethylene | $162 \times 10^{-9}$ | 0.23 | 1.19 | 364 |
| 1,1,2-Trichloroethane | $155 \times 10^{-9}$ | 0.03 | 0.03 | 56 |
| Trichloroethylene | $155 \times 10^{-9}$ | 0.07 | 0.37 | 126 |
| Xylene | $43 \times 10^{-9}$ | 0.10 | 0.22 | 240 |

Having calculated the values in Table 2, the emission rate can now be calculated in terms of grams of VOC per milliliter of air passing through the vadose zone. When converting this emission rate to pounds of VOC per day, assume an air flow equal to 25 cubic feet per minute. This rate corresponds to the injection rate necessary for sparging of the aquifer. The equation becomes:

$$E(lb/day) = E(g/mL) \times (lb/453.6 \text{ g}) \times (1000 \text{ ml}/l) \times (1/0.04 \text{ ft}^3) \times (25 \text{ ft}^3/min) \times (1440 \text{ min/day})$$

## TABLE 3

| Compound | $k_d$, (ml/g) | E, (g/ml) | E, (lb/day) |
|---|---|---|---|
| Tetrachloroethylene | 7.28 | $2.7 \times 10^{-8}$ | $5.4 \times 10^{-2}$ |
| 1,1,2-Trichloroethane | 1.12 | $4.2 \times 10^{-9}$ | $8.4 \times 10^{-2}$ |
| Trichloroethylene | 2.52 | $2.3 \times 10^{-8}$ | $4.6 \times 10^{-2}$ |
| Xylene | 4.80 | $2.0 \times 10^{-9}$ | $4.0 \times 10^{-3}$ |
| **TOTAL** | | $5.6 \times 10^{-8}$ | $1.1 \times 10^{-1}$ |

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